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(21) International Application Number: <b>PCT/US94/12365</b> (22) International Filing Date: <b>27 October 1994 (27.10.94)</b> (30) Priority Data: <b>08/144,980</b> <b>28 October 1993 (28.10.93)</b> <b>US</b> (71) Applicant: <b>CHEVRON CHEMICAL COMPANY (US/US);</b> <b>P.O. Box 7141, San Francisco, CA 94120-7141 (US).</b> (72) Inventor: <b>CHERPECK, Richard, E.; 8962 Cypress Avenue,</b> <b>Cotati, CA 94931 (US).</b> (74) Agents: <b>CAROLI, Claude, J. et al.; Chevron Corporation, Law</b> <b>Dept., P.O. Box 7141, San Francisco, CA 94120-7141 (US).</b>		(81) Designated States: <b>CA, JP, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</b>  Published <i>With international search report.</i>
(54) Title: <b>POLYALKYL HYDROXYAROMATIC ESTERS AND FUEL COMPOSITIONS CONTAINING THE SAME</b>  (57) Abstract <p>Polyalkyl hydroxyaromatic esters having formula (I) or a fuel-soluble salt thereof, where <math>R_1</math> and <math>R_2</math> are independently hydrogen, hydroxy, lower alkyl having 1 to 6 carbon atoms, or lower alkoxy having 1 to 6 carbon atoms; <math>R_3</math> is a polyalkyl group having a weight average molecular weight in the range of about 450 to 5000; and <math>x</math> is an integer from 0 to 10. The polyalkyl hydroxyaromatic esters of formula (I) are useful as fuel additives for the prevention and control of engine deposits.</p> <div data-bbox="915 1522 1705 1779" data-label="Chemical-Block"> </div>		

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01 POLYALKYL HYDROXYAROMATIC ESTERS  
02 AND FUEL COMPOSITIONS CONTAINING THE SAME  
03

04 BACKGROUND OF THE INVENTION  
05

06 Field of the Invention  
07

08 This invention relates to novel hydroxyaromatic compounds.  
09 More particularly, this invention relates to novel polyalkyl  
10 hydroxyaromatic esters and their use in fuel compositions to  
11 prevent and control engine deposits.  
12

13 Description of the Related Art  
14

15 It is well known that automobile engines tend to form  
16 deposits on the surface of engine components, such as  
17 carburetor ports, throttle bodies, fuel injectors, intake  
18 ports and intake valves, due to the oxidation and  
19 polymerization of hydrocarbon fuel. These deposits, even  
20 when present in relatively minor amounts, often cause  
21 noticeable driveability problems, such as stalling and poor  
22 acceleration. Moreover, engine deposits can significantly  
23 increase an automobile's fuel consumption and production of  
24 exhaust pollutants. Therefore, the development of effective  
25 fuel detergents or "deposit control" additives to prevent or  
26 control such deposits is of considerable importance and  
27 numerous such materials are known in the art.  
28

29 For example, aliphatic hydrocarbon-substituted phenols are  
30 known to reduce engine deposits when used in fuel  
31 compositions. U.S. Patent No. 3,849,085, issued  
32 November 19, 1974 to Kreuz et al., discloses a motor fuel  
33 composition comprising a mixture of hydrocarbons in the  
34 gasoline boiling range containing about 0.01 to 0.25 volume

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01 percent of a high molecular weight aliphatic  
02 hydrocarbon-substituted phenol in which the aliphatic  
03 hydrocarbon radical has an average molecular weight in the  
04 range of about 500 to 3,500. This patent teaches that  
05 gasoline compositions containing minor amounts of an  
06 aliphatic hydrocarbon-substituted phenol not only prevent or  
07 inhibit the formation of intake valve and port deposits in a  
08 gasoline engine, but also enhance the performance of the  
09 fuel composition in engines designed to operate at higher  
10 operating temperatures with a minimum of decomposition and  
11 deposit formation in the manifold of the engine.

12  
13 Similarly, U.S. Patent No. 4,134,846, issued January 16,  
14 1979 to Machleder et al., discloses a fuel additive  
15 composition comprising a mixture of (1) the reaction product  
16 of an aliphatic hydrocarbon-substituted phenol,  
17 epichlorohydrin and a primary or secondary mono- or  
18 polyamine, and (2) a polyalkylene phenol. This patent  
19 teaches that such compositions show excellent carburetor,  
20 induction system and combustion chamber detergency and, in  
21 addition, provide effective rust inhibition when used in  
22 hydrocarbon fuels at low concentrations.

23  
24 Amino phenols are also known to function as  
25 detergents/dispersants, antioxidants and anti-corrosion  
26 agents when used in fuel compositions. U.S. Patent  
27 No. 4,320,021, issued March 16, 1982 to R. M. Lange, for  
28 example, discloses amino phenols having at least one  
29 substantially saturated hydrocarbon-based substituent of at  
30 least 30 carbon atoms. The amino phenols of this patent are  
31 taught to impart useful and desirable properties to  
32 oil-based lubricants and normally liquid fuels.

33

34

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01 Nitro phenols have also been employed as fuel additives.  
02 For example, U.S. Patent No. 4,347,148, issued August 31,  
03 1982 to K. E. Davis, discloses nitro phenols containing at  
04 least one aliphatic substituent having at least about 40  
05 carbon atoms. The nitro phenols of this patent are taught  
06 to be useful as detergents, dispersants, antioxidants and  
07 demulsifiers for lubricating oil and fuel compositions.

08

09 In addition, U.S. Patent No. 4,231,759, issued November 4,  
10 1980 to Udelhofen et al., discloses a fuel additive  
11 composition comprising the Mannich condensation product of  
12 (1) a high molecular weight alkyl-substituted  
13 hydroxyaromatic compound wherein the alkyl group has a  
14 number average molecular weight of about 600 to about 3,000,  
15 (2) an amine and (3) an aldehyde. This patent teaches that  
16 such Mannich condensation products provide carburetor  
17 cleanliness when employed alone, and intake valve  
18 cleanliness when employed in combination with a hydrocarbon  
19 carrier fluid.

20

21 U.S. Patent No. 4,859,210, issued August 22, 1989 to Franz  
22 et al., discloses fuel compositions containing (1) one or  
23 more polybutyl or polyisobutyl alcohols wherein the  
24 polybutyl or polyisobutyl group has a number average  
25 molecular weight of 324 to 3,000, or (2) a poly(alkoxylate)  
26 of the polybutyl or polyisobutyl alcohol, or (3) a  
27 carboxylate ester of the polybutyl or polyisobutyl alcohol.  
28 This patent further teaches that when the fuel composition  
29 contains an ester of a polybutyl or polyisobutyl alcohol,  
30 the ester-forming acid group may be derived from saturated  
31 or unsaturated, aliphatic or aromatic, acyclic or cyclic  
32 mono- or polycarboxylic acids.

33

34



01 U.S. Patent No. 3,285,855, issued November 15, 1966 to  
02 Dexter et al., discloses alkyl esters of dialkyl  
03 hydroxybenzoic and hydroxyphenylalkanoic acids wherein the  
04 ester moiety contains from 6 to 30 carbon atoms. This  
05 patent teaches that such esters are useful for stabilizing  
06 polypropylene and other organic material normally subject to  
07 oxidative deterioration. Similar alkyl esters containing  
08 hindered dialkyl hydroxyphenyl groups are disclosed in U.S.  
09 Patent No. 5,196,565, which issued March 23, 1993 to Ross.

10  
11 U.S. Patent No. 5,196,142, issued March 23, 1993 to Mollet  
12 et al., discloses alkyl esters of hydroxyphenyl carboxylic  
13 acids wherein the ester moiety may contain up to 23 carbon  
14 atoms. This patent teaches that such compounds are useful  
15 as antioxidants for stabilizing emulsion-polymerized  
16 polymers.

17  
18 It has now been discovered that certain polyalkyl  
19 hydroxyaromatic esters provide excellent control of engine  
20 deposits, especially intake valve deposits, when employed as  
21 fuel additives in fuel compositions. Moreover, these  
22 polyalkyl hydroxyaromatic esters have been found to produce  
23 fewer combustion chamber deposits than known aliphatic  
24 hydrocarbon-substituted phenolic fuel additives.

25

26

#### SUMMARY OF THE INVENTION

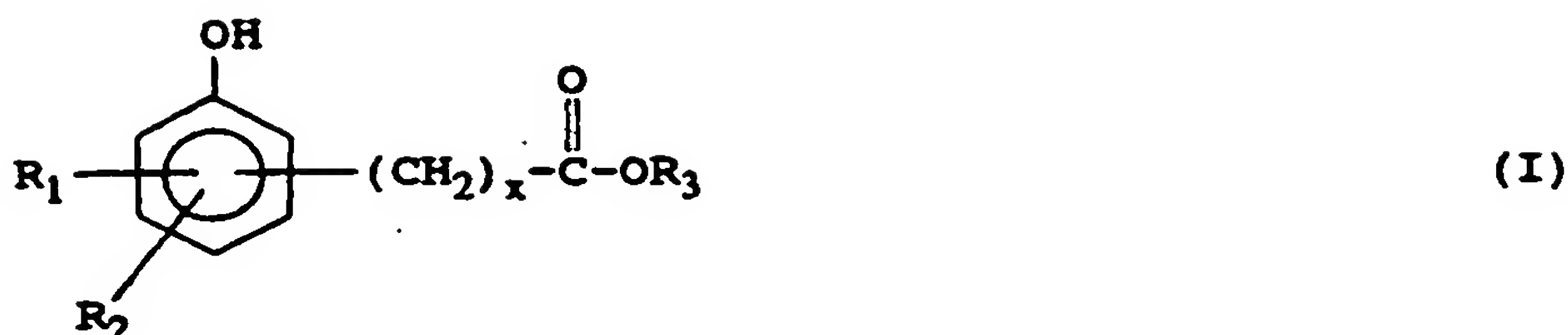
27

28 The present invention provides novel polyalkyl  
29 hydroxyaromatic esters which are useful as fuel additives  
30 for the prevention and control of engine deposits,  
31 particularly intake valve deposits.

32

33 The polyalkyl hydroxyaromatic esters of the present  
34 invention have the formula:

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15 or a fuel-soluble salt thereof; wherein  $R_1$  and  $R_2$  are each  
16 independently hydrogen, hydroxy, lower alkyl having 1 to 6  
17 carbon atoms, or lower alkoxy having 1 to 6 carbon atoms;  $R_3$   
18 is a polyalkyl group having a weight average molecular  
19 weight in the range of about 450 to 5,000; and  $x$  is an  
20 integer from 0 to 10.

21 The present invention further provides a fuel composition  
22 comprising a major amount of hydrocarbons boiling in the  
23 gasoline or diesel range and an effective  
24 deposit-controlling amount of a polyalkyl hydroxyaromatic  
25 ester of the present invention.

26 The present invention additionally provides a fuel  
27 concentrate comprising an inert stable oleophilic organic  
28 solvent boiling in the range of from about 150°F to 400°F  
29 and from about 10 to 70 weight percent of a polyalkyl  
30 hydroxyaromatic ester of the present invention.

31 Among other factors, the present invention is based on the  
32 surprising discovery that certain polyalkyl hydroxyaromatic  
33 esters, when employed as fuel additives in fuel  
34 compositions, provide excellent control of engine deposits,  
especially on intake valves, and produce fewer combustion  
chamber deposits than known aliphatic hydrocarbon-  
substituted phenolic fuel additives.

01                    DETAILED DESCRIPTION OF THE INVENTION

02  
03       The fuel additives provided by the present invention have  
04       the general formula:



13       or a fuel-soluble salt thereof; wherein  $R_1$ ,  $R_2$ ,  $R_3$ , and  $x$   
14       are as defined hereinabove.

15  
16       Preferably,  $R_1$  is hydrogen, hydroxy, or lower alkyl having 1  
17       to 4 carbon atoms. More preferably,  $R_1$  is hydrogen or  
18       hydroxy. Most preferably,  $R_1$  is hydrogen.

19  
20        $R_2$  is preferably hydrogen.

21  
22       Preferably,  $R_3$  is a polyalkyl group having a weight average  
23       molecular weight in the range of about 500 to 5,000, more  
24       preferably about 500 to 3,000, and most preferably about 600  
25       to 2,000.

26  
27       Preferably,  $x$  is an integer from 0 to 2. More preferably,  
28        $x$  is 0.

29  
30       A preferred group of polyalkyl hydroxyaromatic esters are  
31       those of formula I wherein  $R_1$  is hydrogen, hydroxy, or lower  
32       alkyl having 1 to 4 carbon atoms;  $R_2$  is hydrogen; and  $x$   
33       is 0.  
34



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01 Another preferred group of polyalkyl hydroxyaromatic esters  
02 are those of formula I wherein  $R_1$  is hydrogen, hydroxy, or  
03 lower alkyl having 1 to 4 carbon atoms;  $R_2$  is hydrogen; and  
04  $x$  is 1 or 2.  
05

06 A more preferred group of polyalkyl hydroxyaromatic esters  
07 are those of formula I wherein  $R_1$  is hydrogen or hydroxy;  $R_2$   
08 is hydrogen; and  $x$  is 0.  
09

10 It is especially preferred that the aromatic hydroxyl group  
11 or groups present in the polyalkyl hydroxyaromatic esters of  
12 this invention be situated in a meta or para position  
13 relative to the polyalkyl ester moiety. When the aromatic  
14 moiety contains one hydroxyl group, it is particularly  
15 preferred that this hydroxyl group be in a para position  
16 relative to the polyalkyl ester moiety.  
17

18 The polyalkyl hydroxyaromatic esters of the present  
19 invention will generally have a sufficient molecular weight  
20 so as to be non-volatile at normal engine intake valve  
21 operating temperatures (about 200-250°C). Typically, the  
22 molecular weight of the polyalkyl hydroxyaromatic esters of  
23 this invention will range from about 600 to about 6,000,  
24 preferably from 600 to 3,000, more preferably from 700 to  
25 2,000.  
26

27 Fuel-soluble salts of the polyalkyl hydroxyaromatic esters  
28 of the present invention are also contemplated to be useful  
29 for preventing or controlling deposits. Such salts include  
30 alkali metal, alkaline earth metal, ammonium, substituted  
31 ammonium and sulfonium salts. Preferred metal salts are the  
32 alkali metal salts, particularly the sodium and potassium  
33 salts, and the substituted ammonium salts, particularly  
34

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01 tetraalkyl-substituted ammonium salts, such as the  
02 tetrabutylammonium salts.

03

04 Definitions

05

06 As used herein, the following terms have the following  
07 meanings unless expressly stated to the contrary.

08

09 The term "alkyl" refers to both straight- and branched-chain  
10 alkyl groups.

11

12 The term "lower alkyl" refers to alkyl groups having 1 to  
13 about 6 carbon atoms and includes primary, secondary and  
14 tertiary alkyl groups. Typical lower alkyl groups include,  
15 for example, methyl, ethyl, n-propyl, isopropyl, n-butyl,  
16 sec-butyl, t-butyl, n-pentyl, n-hexyl and the like.

17

18 The term "lower alkoxy" refers to the group  $-OR_x$  wherein  $R_x$   
19 is lower alkyl. Typical lower alkoxy groups include  
20 methoxy, ethoxy, and the like.

21

22 The term "polyalkyl" refers to alkyl groups which are  
23 generally derived from polyolefins which are polymers or  
24 copolymers of mono-olefins, particularly 1-mono-olefins,  
25 such as ethylene, propylene, butylene, and the like.  
26 Preferably, the mono-olefin employed will have 2 to about  
27 24 carbon atoms, and more preferably, about 3 to 12 carbon  
28 atoms. More preferred mono-olefins include propylene,  
29 butylene, particularly isobutylene, 1-octene and 1-decene.  
30 Polyolefins prepared from such mono-olefins include  
31 polypropylene, polybutene, especially polyisobutene, and the  
32 polyalphaolefins produced from 1-octene and 1-decene.

33

34

01 General Synthetic Procedures

02

03 The polyalkyl hydroxyaromatic esters of this invention may  
04 be prepared by the following general methods and procedures.  
05 It should be appreciated that where typical or preferred  
06 process conditions (e.g., reaction temperatures, times, mole  
07 ratios of reactants, solvents, pressures, etc.) are given,  
08 other process conditions may also be used unless otherwise  
09 stated. Optimum reaction conditions may vary with the  
10 particular reactants or solvents used, but such conditions  
11 can be determined by one skilled in the art by routine  
12 optimization procedures.

13

14 Moreover, those skilled in the art will recognize that it  
15 may be necessary to block or protect certain functional  
16 groups while conducting the following synthetic procedures.  
17 In such cases, the protecting group will serve to protect  
18 the functional group from undesired reactions or to block  
19 its undesired reaction with other functional groups or with  
20 the reagents used to carry out the desired chemical  
21 transformations. The proper choice of a protecting group  
22 for a particular functional group will be readily apparent  
23 to one skilled in the art. Various protecting groups and  
24 their introduction and removal are described, for example,  
25 in T. W. Greene and P. G. M. Wuts, *Protective Groups in*  
26 *Organic Synthesis*, Second Edition, Wiley, New York, 1991,  
27 and references cited therein.

28

29 In the present synthetic procedures, a hydroxyl group will  
30 preferably be protected, when necessary, as the benzyl or  
31 tert-butyldimethylsilyl ether. Introduction and removal of  
32 these protecting groups is well described in the art.

33

34

01 The polyalkyl hydroxyaromatic esters of the present  
02 invention having the formula:

03

04

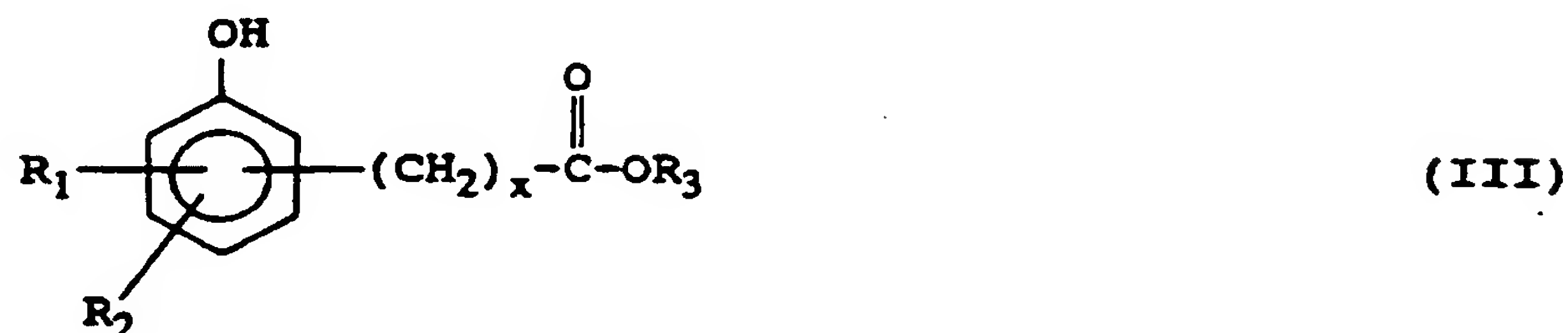
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08

09



10

11

12

13

wherein  $\text{R}_1$ ,  $\text{R}_2$ ,  $\text{R}_3$  and  $x$  are as defined above, may be  
prepared by esterifying a hydroxyaromatic carboxylic acid  
having the formula:

14

15

16

17

18

19



20

21

22

23

wherein  $\text{R}_1$ ,  $\text{R}_2$ , and  $x$  are as defined above, with a polyalkyl  
alcohol having the formula:

24

25



26

27

28

wherein  $\text{R}_3$  is as defined above, using conventional  
esterification reaction conditions.

29

30

31

32

33

34

The hydroxyaromatic carboxylic acids of formula IV are  
either known compounds or can be prepared from known  
compounds by conventional procedures. Suitable  
hydroxyaromatic carboxylic acids for use as starting  
materials in this invention are 2-hydroxybenzoic acid,

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01 3-hydroxybenzoic acid, 4-hydroxybenzoic acid,  
02 3,4-dihydroxybenzoic acid, 3,4,5-trihydroxybenzoic acid,  
03 3-hydroxy-4-methoxybenzoic acid, 4-hydroxy-3-methoxybenzoic  
04 acid, 3-t-butyl-4-hydroxybenzoic acid, 3,5-di-t-butyl-4-  
05 hydroxybenzoic acid, 4-hydroxyphenylacetic acid,  
06 3-(4-hydroxyphenyl)propionic acid and the like.

07

08 The polyalkyl alcohols of formula V may also be prepared by  
09 conventional procedures known in the art. Such procedures  
10 are taught, for example, in U.S. Patent Nos. 5,055,607 to  
11 Buckley and 4,859,210 to Franz et al., the disclosures of  
12 which are incorporated herein by reference.

13

14 In general, the polyalkyl substituent on the polyalkyl  
15 alcohols of Formula V and the resulting polyalkyl  
16 hydroxyaromatic esters of the present invention will have a  
17 weight average molecular weight in the range of about 450 to  
18 5,000, preferably about 500 to 5,000, more preferably about  
19 500 to 3,000, and most preferably about 600 to 2,000.

20

21 The polyalkyl substituent on the polyalkyl alcohols employed  
22 in the invention may be generally derived from polyolefins  
23 which are polymers or copolymers of mono-olefins,  
24 particularly 1-mono-olefins, such as ethylene, propylene,  
25 butylene, and the like. Preferably, the mono-olefin  
26 employed will have 2 to about 24 carbon atoms, and more  
27 preferably, about 3 to 12 carbon atoms. More preferred  
28 mono-olefins include propylene, butylene, particularly  
29 isobutylene, 1-octene and 1-decene. Polyolefins prepared  
30 from such mono-olefins include polypropylene, polybutene,  
31 especially polyisobutene, and the polyalphaolefins produced  
32 from 1-octene and 1-decene.

33

34



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01 The preferred polyisobutenes used to prepare the presently  
02 employed polyalkyl alcohols are polyisobutenes which  
03 comprise at least about 20% of the more reactive  
04 methylvinylidene isomer, preferably at least 50% and more  
05 preferably at least 70%. Suitable polyisobutenes include  
06 those prepared using BF<sub>3</sub> catalysts. The preparation of such  
07 polyisobutenes in which the methylvinylidene isomer  
08 comprises a high percentage of the total composition is  
09 described in U.S. Patent Nos. 4,152,499 and 4,605,808. Such  
10 polyisobutenes, known as "reactive" polyisobutenes, yield  
11 high molecular weight alcohols in which the hydroxyl group  
12 is at or near the end of the hydrocarbon chain.

13

14 Examples of suitable polyisobutenes having a high  
15 alkylvinylidene content include Ultravis 30, a polyisobutene  
16 having a molecular weight of about 1300 and a  
17 methylvinylidene content of about 74%, and Ultravis 10, a  
18 polyisobutene having a molecular weight of about 950 and a  
19 methylvinylidene content of about 76%, both available from  
20 British Petroleum.

21

22 The polyalkyl alcohols may be prepared from the  
23 corresponding olefins by conventional procedures. Such  
24 procedures include hydration of the double bond to give an  
25 alcohol. Suitable procedures for preparing such long-chain  
26 alcohols are described in I. T. Harrison and S. Harrison,  
27 *Compendium of Organic Synthetic Methods*, Wiley-Interscience,  
28 New York (1971), pp. 119-122, as well as in U.S. Patent  
29 Nos. 5,055,607 and 4,859,210.

30

31 As indicated above, the polyalkyl hydroxyaromatic esters of  
32 formula III may be prepared by esterifying a hydroxyaromatic  
33 carboxylic acid of formula IV with a polyalkyl alcohol of  
34

-13-

01 formula V under conventional esterification reaction  
02 conditions.

03

04 Typically, this reaction will be conducted by contacting a  
05 polyalkyl alcohol of formula V with about 0.25 to about 1.5  
06 molar equivalents of a hydroxyaromatic carboxylic acid of  
07 formula IV in the presence of an acidic catalyst at a  
08 temperature in the range of about 70°C to about 160°C for  
09 about 0.5 to about 48 hours. Suitable acid catalysts for  
10 this reaction include p-toluene sulfonic acid,  
11 methanesulfonic acid and the like. The reaction may be  
12 conducted in the presence or absence of an inert solvent,  
13 such as benzene, toluene and the like. The water generated  
14 by this reaction is preferably removed during the course of  
15 the reaction by, for example, azeotropic distillation with  
16 an inert solvent, such as toluene.

17

18 The polyalkyl hydroxyaromatic esters of formula III may also  
19 be synthesized by reacting a polyalkyl alcohol of formula V  
20 with an acyl halide having the formula:

21

22

23

24

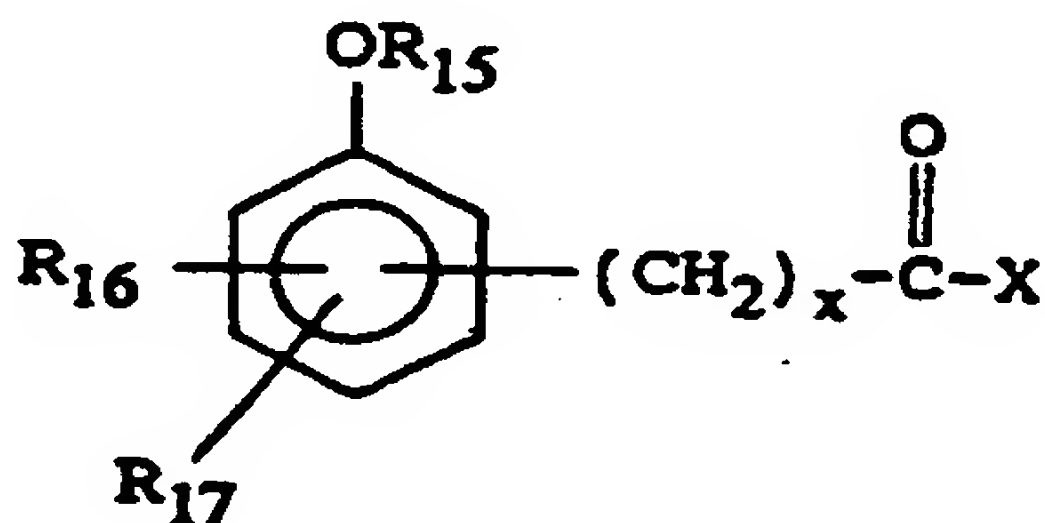
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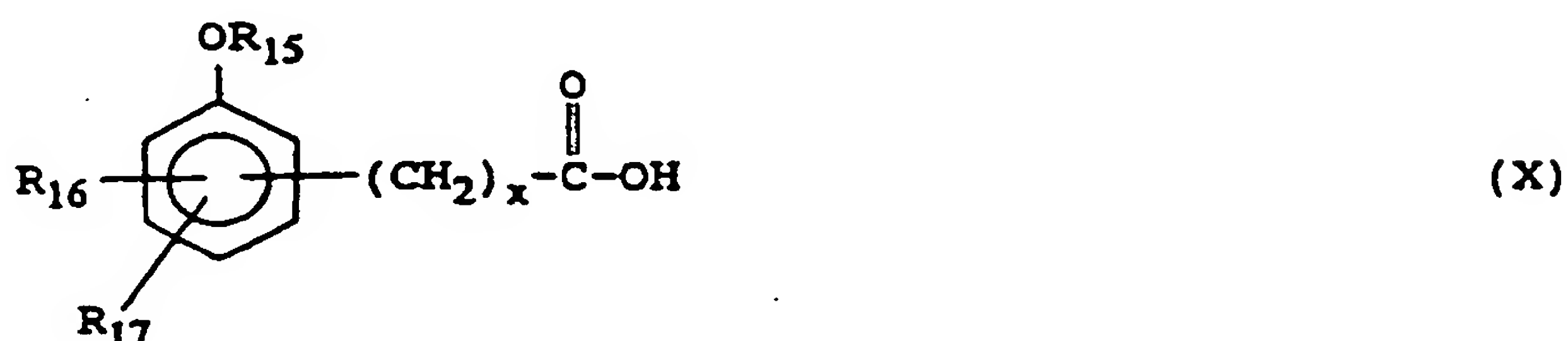
29 wherein X is a halide, such as chloride or bromide, and R<sub>15</sub>  
30 is a suitable hydroxyl protecting group, such as benzyl,  
31 tert-butyldimethylsilyl, methoxymethyl, and the like; R<sub>16</sub>  
32 and R<sub>17</sub> are each independently hydrogen, lower alkyl, lower  
33 alkoxy, or the group -OR<sub>18</sub>, wherein R<sub>18</sub> is a suitable  
34 hydroxyl protecting group.



(IX)

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01 Acyl halides of formula IX may be prepared from the  
02 hydroxyaromatic carboxylic acids of formula IV by first  
03 protecting the aromatic hydroxyl groups of formula IV to  
04 form a carboxylic acid having the formula:



13 wherein  $R_{15}$ - $R_{17}$  and  $x$  are as defined above, and then  
14 converting the carboxylic acid moiety of formula X into an  
15 acyl halide using conventional procedures.

16 Protection of the aromatic hydroxyl groups of formula IV may  
17 be accomplished using well known procedures. The choice of  
18 a suitable protecting group for a particular hydroxyaromatic  
19 carboxylic acid will be apparent to those skilled in the  
20 art. Various protecting groups, and their introduction and  
21 removal, are described, for example, in T. W. Greene and  
22 P. G. M. Wuts, *Protective Groups in Organic Synthesis*,  
23 Second Edition, Wiley, New York, 1991, and references cited  
24 therein. Alternatively, the protected derivatives of  
25 formula X can be prepared from known starting materials  
26 other than the hydroxyaromatic compounds of formula IV by  
27 conventional procedures.  
28

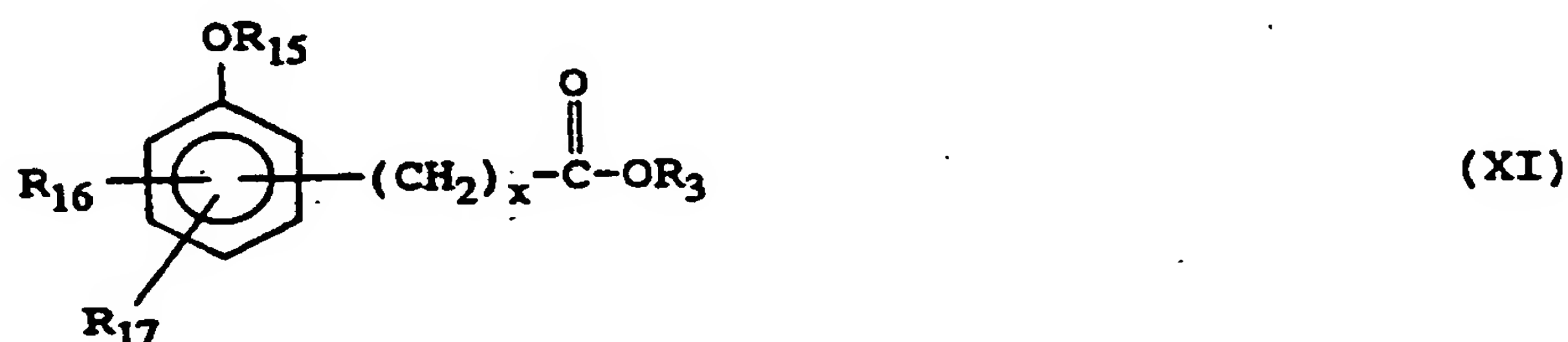
29 The carboxylic acid moiety of formula X may be converted  
30 into an acyl halide by contacting a compound of formula X  
31 with an inorganic acid halide, such as thionyl chloride,  
32 phosphorous trichloride, phosphorous tribromide, or  
33 phosphorous pentachloride; or alternatively, with oxalyl  
34

-15-

01 chloride. Generally, this reaction will be conducted using  
02 about 1 to 5 molar equivalents of the inorganic acid halide  
03 or oxalyl chloride, either neat or in an inert solvent, such  
04 as diethyl ether, at a temperature in the range of about  
05 20°C to about 80°C for about 1 to about 48 hours. A  
06 catalyst, such as N,N-dimethylformamide, may also be used in  
07 this reaction.

08  
09 In certain cases where the hydroxyaromatic carboxylic acids  
10 of formula IV having bulky alkyl groups adjacent to the  
11 hydroxyl group, such as 3,5-di-t-butyl-4-hydroxybenzoic  
12 acid, it will generally not be necessary to protect the  
13 hydroxyl group prior to formation of the acyl halide, since  
14 such hydroxyl groups are sufficiently sterically hindered so  
15 as to be substantially non-reactive with the acyl halide  
16 moiety.

17  
18 Reaction of an acyl halide of formula IX with a polyalkyl  
19 alcohol of formula V provides an intermediate polyalkyl  
20 ester having the formula:



28 wherein  $\text{R}_3$ ,  $\text{R}_{15}$ - $\text{R}_{17}$ , and  $x$  are as defined above.

29  
30 Typically, this reaction is conducted by contacting an  
31 alcohol of formula V with about 0.9 to about 1.5 molar  
32 equivalents of an acyl halide of formula IX in an inert  
33 solvent, such as toluene, dichloromethane, diethyl ether,  
34



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01 and the like, at a temperature in the range of about 25°C to  
02 about 150°C. The reaction is generally complete in about  
03 0.5 to about 48 hours. Preferably, the reaction is  
04 conducted in the presence of a sufficient amount of an amine  
05 capable of neutralizing the acid generated during the  
06 reaction, such as triethylamine, di(isopropyl)ethylamine,  
07 pyridine or 4-dimethylamino-pyridine.

08

09 Deprotection of the aromatic hydroxyl group(s) on the esters  
10 of formula XI then provides a polyalkyl hydroxyaromatic  
11 ester of formula III. Appropriate conditions for this  
12 deprotection step will depend upon the protecting group(s)  
13 utilized in the synthesis and will be readily apparent to  
14 those skilled in the art. For example, benzyl protecting  
15 groups may be removed by hydrogenolysis under 1 to about 4  
16 atmospheres of hydrogen in the presence of a catalyst, such  
17 as palladium on carbon. Typically, this deprotection  
18 reaction is conducted in an inert solvent, preferably a  
19 mixture of ethyl acetate and acetic acid, at a temperature  
20 of from about 0°C to about 40°C for about 1 to about  
21 24 hours.

22

23

#### Fuel Compositions

24

25 The polyalkyl hydroxyaromatic esters of the present  
26 invention are useful as additives in hydrocarbon fuels to  
27 prevent and control engine deposits, particularly intake  
28 valve deposits. The proper concentration of additive  
29 necessary to achieve the desired deposit control varies  
30 depending upon the type of fuel employed, the type of  
31 engine, and the presence of other fuel additives.

32

33 In general, the concentration of the polyalkyl  
34 hydroxyaromatic esters of this invention in hydrocarbon fuel



-17-

01 will range from about 50 to about 2500 parts per million  
02 (ppm) by weight, preferably from 75 to 1,000 ppm. When  
03 other deposit control additives are present, a lesser amount  
04 of the present additive may be used.  
05

06 The polyalkyl hydroxyaromatic esters of the present  
07 invention may be formulated as a concentrate using an inert  
08 stable oleophilic (i.e., dissolves in gasoline) organic  
09 solvent boiling in the range of about 150°F to 400°F (about  
10 65°C to 205°C). Preferably, an aliphatic or an aromatic  
11 hydrocarbon solvent is used, such as benzene, toluene,  
12 xylene or higher-boiling aromatics or aromatic thinners.  
13 Aliphatic alcohols containing about 3 to 8 carbon atoms,  
14 such as isopropanol, isobutylcarbinol, n-butanol and the  
15 like, in combination with hydrocarbon solvents are also  
16 suitable for use with the present additives. In the  
17 concentrate, the amount of the additive will generally range  
18 from about 10 to about 70 weight percent, preferably 10 to  
19 50 weight percent, more preferably from 20 to 40 weight  
20 percent.  
21

22 In gasoline fuels, other fuel additives may be employed with  
23 the additives of the present invention, including, for  
24 example, oxygenates, such as t-butyl methyl ether, antiknock  
25 agents, such as methylcyclopentadienyl manganese  
26 tricarbonyl, and other dispersants/detergents, such as  
27 hydrocarbyl amines, hydrocarbyl poly(oxyalkylene) amines, or  
28 succinimides. Additionally, antioxidants, metal  
29 deactivators and demulsifiers may be present.  
30

31 In diesel fuels, other well-known additives can be employed,  
32 such as pour point depressants, flow improvers, cetane  
33 improvers, and the like.  
34

-18-

01 A fuel-soluble, nonvolatile carrier fluid or oil may also be  
02 used with the polyalkyl hydroxyaromatic esters of this  
03 invention. The carrier fluid is a chemically inert  
04 hydrocarbon-soluble liquid vehicle which substantially  
05 increases the nonvolatile residue (NVR), or solvent-free  
06 liquid fraction of the fuel additive composition while not  
07 overwhelmingly contributing to octane requirement increase.  
08 The carrier fluid may be a natural or synthetic oil, such as  
09 mineral oil, refined petroleum oils, synthetic polyalkanes  
10 and alkenes, including hydrogenated and unhydrogenated  
11 polyalphaolefins, and synthetic polyoxyalkylene-derived  
12 oils, such as those described, for example, in U.S. Patent  
13 No. 4,191,537 to Lewis, and polyesters, such as those  
14 described, for example, in U.S. Patent Nos. 3,756,793 and  
15 5,004,478 to Robinson and Vogel et al., respectively, and in  
16 European Patent Application Nos. 356,726 and 382,159,  
17 published March 7, 1990 and August 16, 1990, respectively.

18  
19 These carrier fluids are believed to act as a carrier for  
20 the fuel additives of the present invention and to assist in  
21 removing and retarding deposits. The carrier fluid may also  
22 exhibit synergistic deposit control properties when used in  
23 combination with a hydroxyaromatic polyalkyl compound of  
24 this invention.

25  
26 The carrier fluids are typically employed in amounts ranging  
27 from about 100 to about 5000 ppm by weight of the  
28 hydrocarbon fuel, preferably from 400 to 3000 ppm of the  
29 fuel. Preferably, the ratio of carrier fluid to deposit  
30 control additive will range from about 0.5:1 to about 10:1,  
31 more preferably from 1:1 to 4:1, most preferably about 2:1.

32  
33 When employed in a fuel concentrate, carrier fluids will  
34 generally be present in amounts ranging from about 20 to

-19-

01 about 60 weight percent, preferably from 30 to 50 weight  
02 percent.

03

04

EXAMPLES

05

06 The following examples are presented to illustrate specific  
07 embodiments of the present invention and synthetic  
08 preparations thereof; and should not be interpreted as  
09 limitations upon the scope of the invention.

10

11

Example 1

12

13

Preparation of Polyisobutyl 4-Hydroxybenzoate

14

15 To a flask equipped with a mechanical stirrer, thermometer,  
16 Dean Stark trap, reflux condensor and nitrogen inlet was  
17 added 525 grams of polyisobutanol (molecular weight average  
18 984, prepared via hydroformylation of Amoco H-100  
19 polyisobutene), 124.7 grams of 4-hydroxybenzoic acid, and  
20 13.0 grams of p-toluene sulfonic acid. The mixture was  
21 stirred at 130°C for sixteen hours, cooled to room  
22 temperature and diluted with 2 liters of diethyl ether. The  
23 organic phase was washed two times with saturated aqueous  
24 sodium bicarbonate, once with brine, dried over anhydrous  
25 magnesium sulfate, filtered and concentrated in vacuo to  
26 yield 514.3 grams of the desired product as a yellow oil.  
27 IR (neat) 1715, 1685  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.95 (d, 2H), 6.9  
28 (d, 2H), 5.8 (bs, 1H), 4.3 (t, 2H), 0.6-1.8 (m, 137H).

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-20-

Example 2Preparation of Polyisobutyl 4-Hydroxyphenylacetate

To a flask equipped with a mechanical stirrer, thermometer, Dean Stark trap, reflux condensor and nitrogen inlet was added 35.0 grams of polyisobutanol (molecular weight average 984, prepared via hydroformylation of Amoco H-100 polyisobutene), 9.16 grams of 4-hydroxyphenylacetic acid, and 0.86 grams of p-toluene sulfonic acid. The mixture was stirred at 130°C for sixteen hours, cooled to room temperature and diluted with 500 milliliters of diethyl ether. The organic phase was washed three times with methanol/water (4:1), once with brine, dried over anhydrous magnesium sulfate, filtered and concentrated in vacuo to yield 45.8 grams of a brown oil. The oil was chromatographed on silica gel eluting with hexane/ethyl acetate/ethanol (8:1.8:0.2) to yield 26.6 grams of the desired product as a yellow oil. IR (neat) 1714  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.15 (d, 2H), 6.75 (d, 2H), 5.05 (bs, 1H), 4.1 (t, 2H), 3.5 (s, 2H), 0.6-1.8 (m, 137H).

Example 3Preparation of Polyisobutyl Salicylate

To a flask equipped with a mechanical stirrer, thermometer, Dean Stark trap, reflux condensor and nitrogen inlet was added 35.0 grams of polyisobutanol (molecular weight average 984, prepared via hydroformylation of Amoco H-100 polyisobutene), 8.3 grams of salicylic acid, and 0.86 grams of p-toluene sulfonic acid. The mixture was stirred at 130°C for sixteen hours, cooled to room temperature and



-21-

01 diluted with 500 milliliters of diethyl ether. The organic  
02 phase was washed three times with methanol/water (4:1), once  
03 with brine, dried over anhydrous magnesium sulfate, filtered  
04 and concentrated in vacuo to yield 43.3 grams of a yellow  
05 oil. The oil was chromatographed on silica gel eluting with  
06 hexane/ethyl acetate/ethanol (8:1.8:0.2) to yield 26.4 grams  
07 of the desired product as a yellow oil. IR (neat)  
08 1682  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  10.8 (s, 1H), 7.8 (d, 1H), 7.4  
09 (t, 1H), 7.0 (d, 1H), 6.8 (t, 1H), 4.3 (t, 2H), 0.6-1.8 (m,  
10 137H).

11

12

#### Example 4

13

#### 14 Preparation of 4-Benzyloxy-2,6-dimethylbenzoyl Chloride

15

16 To a flask equipped with a magnetic stirrer and nitrogen  
17 inlet was added 11.35 grams of 4-benzyloxy-2,6-  
18 dimethylbenzoic acid (prepared as described by S. Thea,  
19 G. Cevasco, G. Guanti, No. Kashefi-Naini and A. Williams,  
20 J. Org. Chem., 50, 1867 (1985)), 120 mL of anhydrous  
21 methylene chloride, followed by 9.7 mL of oxalyl chloride.  
22 The resulting mixture was stirred at room temperature for  
23 16 hours and then the solvent was removed in vacuo to yield  
24 11.4 grams of the desired acid chloride.

25

26

#### Example 5

27

#### 28 Preparation of Polyisobutyl 4-Benzyloxy-2,6-dimethylbenzoate

29

30 4-Benzyloxy-2,6-dimethylbenzoyl chloride (5.3 grams) from  
31 Example 4 was combined with 13.5 grams of polyisobutanol  
32 (molecular weight average 984, prepared via hydroformylation  
33 of Amoco H-100 polyisobutene) and 200 mL of anhydrous

34



-22-

01 toluene. Triethylamine (2.8 mL) and 4-dimethylaminopyridine  
02 (1.18 grams) were then added and the resulting mixture was  
03 heated to reflux under nitrogen for 16 hours. The reaction  
04 was cooled to room temperature and diluted with diethyl  
05 ether. The organic layer was washed twice with 1% aqueous  
06 hydrochloric acid, twice with saturated aqueous sodium  
07 bicarbonate solution, and once with brine. The organic  
08 layer was then dried over anhydrous magnesium sulfate,  
09 filtered and the solvents removed in vacuo to yield  
10 17.8 grams of a brown oil. The oil was chromatographed on  
11 silica gel, eluting with hexane/ethyl acetate/ethanol  
12 (9:0.8:0.2), to yield 16.8 grams of the desired product as a  
13 brown oil.

14

15

Example 6

16

Preparation of Polyisobutyl 4-Hydroxy-2,6-dimethylbenzoate

18

19 A solution of 16.8 grams of the product from Example 5 in  
20 100 mL of ethylacetate and 100 mL of acetic acid containing  
21 3.0 grams of 10% palladium on charcoal was hydrogenolyzed at  
22 35-40 psi for 16 hours on a Parr low-pressure hydrogenator.  
23 Catalyst filtration and removal of residual acetic acid with  
24 toluene in vacuo yielded 13.6 grams of the desired product  
25 as a yellow oil. IR (neat) 1729, 1696  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$   
26 6.5 (s, 2H), 5.0 (bs, 1H), 4.3 (t, 2H), 2.3 (s, 6H), 0.6-1.8  
27 (m, 137H).

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-23-

01

Example 7

02

03

Preparation of Polyisobutanol via Hydroboration

04

05 Polyisobutene (molecular weight average 700, available from  
06 Exxon as Parapol 700, 100 grams) was combined with anhydrous  
07 tetrahydrofuran (1.0 L) and cooled to 0°C under nitrogen.  
08 Borane-tetrahydrofuran complex (157 mL of a 1 M solution  
09 of borane in tetrahydrofuran) was added dropwise and then  
10 the reaction was allowed to warm to room temperature and  
11 stirred for sixteen hours. 143 mL of 3 N aqueous sodium  
12 hydroxide was added dropwise followed by 52.5 mL of 30%  
13 aqueous hydrogen peroxide. The mixture was stirred at room  
14 temperature for one hour and then diluted with 2.0 L of  
15 diethyl ether. The organic phase was washed three times  
16 with water, once with brine, dried over anhydrous magnesium  
17 sulfate, filtered and concentrated in vacuo to yield  
18 96.4 grams of a yellow oil. The oil was chromatographed on  
19 silica gel eluting with hexane followed by hexane/ethyl  
20 acetate/ethanol (9:0.8:0.2) to yield 91 grams of the desired  
21 product as a light yellow oil.

22

23

Example 8

24

25

Preparation of 4-Benzyloxybenzoyl Chloride

26

27 To a flash equipped with a magnetic stirrer and drying tube  
28 was added 75.0 grams of 4-benzyloxybenzoic acid and 700 mL  
29 of anhydrous methylene chloride and then 72 mL of oxalyl  
30 chloride. The resulting mixture was stirred at room  
31 temperature for 16 hours and then the solvent was removed in  
32 vacuo to yield 79.6 grams of the desired acid chloride.

33

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-24-

01

Example 9

02

03

Preparation of Polyisobutyl 4-Benzyloxybenzoate

04

05 4-Benzyloxybenzoyl chloride (6.9 grams) from Example 8 was  
06 combined with 20.0 grams of polyisobutanol from Example 7  
07 and 200 mL of toluene. Triethylamine (4.1 mL) and  
08 4-dimethylaminopyridine (1.70 grams) were then added and the  
09 resulting mixture was heated to reflux for 16 hours. The  
10 reaction was cooled to room temperature and diluted with  
11 diethyl ether. The organic layer was washed twice with 1%  
12 aqueous hydrochloric acid, twice with saturated aqueous sodium  
13 bicarbonate solution, and once with brine. The organic  
14 layer was then dried over anhydrous magnesium sulfate,  
15 filtered and the solvents removed in vacuo to yield  
16 24.9 grams of a yellow oil. The oil was chromatographed on  
17 silica gel eluting with hexane/diethyl ether/ethanol  
18 (9:0.8:0.2), to yield 20.6 grams of the desired product as a  
19 light yellow oil.

20

21

Example 10

22

23

Preparation of Polyisobutyl 4-Hydroxybenzoate  
from Hydroborated Polyisobutene

24

25

26 A solution of 20.6 grams of the product from Example 9 in  
27 100 mL of ethylacetate and 100 mL of acetic acid containing  
28 3.0 grams of 10% palladium on charcoal was hydrogenolyzed at  
29 35-40 psi for 16 hours on a Parr low-pressure hydrogenator.  
30 Catalyst filtration and removal of residual acetic acid with  
31 toluene in vacuo yielded 19.2 grams of the desired product  
32 as a light yellow oil. IR (neat) 1716, 1682  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR

33

34

-25-

01 (CDCl<sub>3</sub>) δ 8.0 (d, 2H), 6.9 (d, 2H), 5.1 (m, 1H), 0.6-1.8  
02 (m, 96H).  
03

04 Example 11  
05

06 Single-Cylinder Engine Test  
07

08 The test compounds were blended in gasoline and their  
09 deposit reducing capacity determined in an ASTM/CFR  
10 single-cylinder engine test.  
11

12 A Waukesha CFR single-cylinder engine was used. Each run  
13 was carried out for 15 hours, at the end of which time the  
14 intake valve was removed, washed with hexane and weighed.  
15 The previously determined weight of the clean valve was  
16 subtracted from the weight of the valve at the end of the  
17 run. The differences between the two weights is the weight  
18 of the deposit. A lesser amount of deposit indicates a  
19 superior additive. The operating conditions of the test  
20 were as follows: water jacket temperature 200°F; vacuum of  
21 12 in Hg, air-fuel ratio of 12, ignition spark timing of  
22 40° BTC; engine speed is 1800 rpm; the crankcase oil is a  
23 commercial 30W oil.  
24

25 The amount of carbonaceous deposit in milligrams on the  
26 intake valves is reported for each of the test compounds in  
27 Table I and Table II.  
28  
29  
30  
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33  
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-26-

TABLE I

Intake Valve Deposit Weight  
(in milligrams)

Sample <sup>1</sup>	Run 1	Run 2	Average
Base Fuel	164.4	158.1	161.3
Example 1	27.0	35.0	31.0
Example 6	17.2	12.2	14.7
Example 10	7.0	7.6	7.3

<sup>1</sup>At 200 parts per million actives (ppma).

TABLE II

Intake Valve Deposit Weight  
(in milligrams)

Sample <sup>1</sup>	Run 1	Run 2	Average
Base Fuel	302.6	312.2	307.4
Example 2	68.9	57.4	63.2
Example 3	272.0	232.7	252.4

<sup>1</sup>At 200 parts per million actives (ppma).

The base fuel employed in the above single-cylinder engine tests was a regular octane unleaded gasoline containing no fuel detergent. The test compounds were admixed with the base fuel to give a concentration of 200 ppma (parts per million actives).

The data in Table I and Table II illustrates the significant reduction in intake valve deposits provided by the polyalkyl hydroxyaromatic esters of the present invention (Examples 1, 2, 3, 6 and 10) compared to the base fuel.



-27-

Example 12Multicylinder Engine Test

The polyalkyl hydroxyaromatic esters of the present invention were tested in a laboratory multicylinder engine to evaluate their intake valve and combustion chamber deposit control performance. The test engine was a 4.3 liter, TBI (throttle body injected), V6 engine manufactured by General Motors Corporation.

The major engine dimensions are set forth in Table III:

Table III

Engine Dimensions

Bore	10.16 cm
Stroke	8.84 cm
Displacement Volume	4.3 liter
Compression Ratio	9.3:1

The test engine was operated for 40 hours (24 hours a day) on a prescribed load and speed schedule representative of typical driving conditions. The cycle for engine operation during the test is set forth in Table IV.

-28-

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Table IV

Engine Driving Cycle

Step	Mode	Time in Mode [Sec] <sup>1</sup>	Dynamometer Load [kg]	Engine Speed [RPM]
1	Idle	60	0	800
2	City Cruise	150	10	1,500
3	Acceleration	40	25	2,800
4	Heavy HWY Cruise	210	15	2,200
5	Light HWY Cruise	60	10	2,200
6	Idle	60	0	800
7	City Cruise	180	10	1,500
8	Idle	60	0	800

<sup>1</sup> All steps, except step number 3, include a 15 second transition ramp. Step 3 includes a 20 second transition ramp.

All of the test runs were made with the same base gasoline, which was representative of commercial unleaded fuel. The results are set forth in Table V.

-29-

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Table V  
Multicylinder Engine Test Results

Sample <sup>1</sup>		Intake Valve Deposits <sup>2</sup>	Combustion Chamber Deposits <sup>2</sup>
Base Fuel	Run 1	710	2339
	Run 2	962	2059
	Average	836	2199
Example 1	Run 1	238	2317
	Run 2	292	2418
	Average	265	2368

<sup>1</sup>At 200 parts per million actives (ppma).

<sup>2</sup>In milligrams (mg).

The base fuel employed in the above multicylinder engine tests contained no fuel detergent. The test compounds were admixed with the base fuel to give a concentration of 200 ppma (parts per million actives).

The data in Table V illustrates the significant reduction in intake valve deposits provided by the polyalkyl hydroxyaromatic esters of the present invention (Example 1) compared to the base fuel. Moreover, the data in Table V further demonstrates that the polyalkyl hydroxyaromatic esters of the present invention do not contribute significantly to combustion chamber deposits.

-30-

01 WHAT IS CLAIMED IS:

02

03 1. A compound of the formula:

04

05

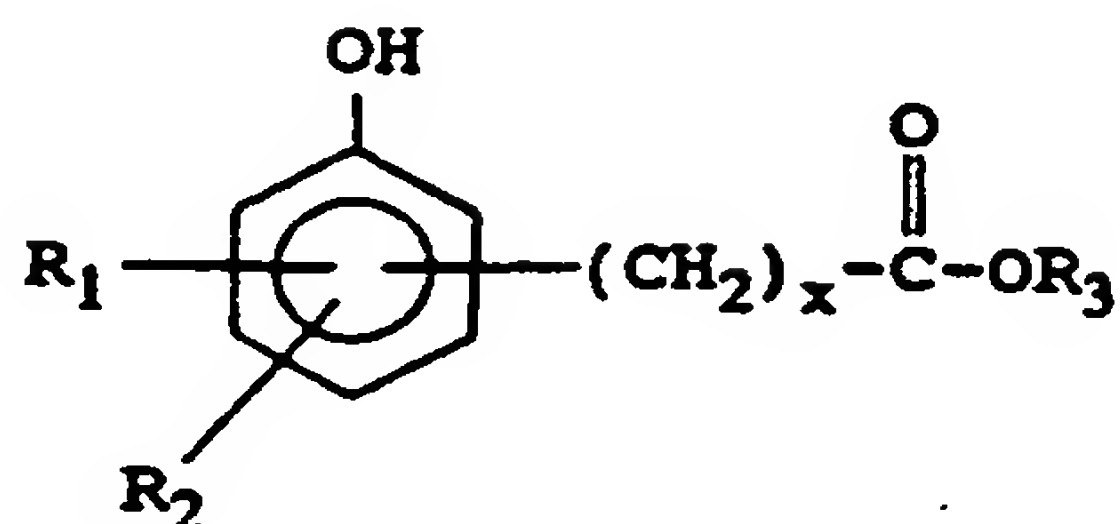
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11

12

or a fuel-soluble salt thereof; wherein

13

14

15

16

R<sub>1</sub> and R<sub>2</sub> are independently hydrogen, hydroxy, lower alkyl having 1 to 6 carbon atoms, or lower alkoxy having 1 to 6 carbon atoms;

17

18

19

20

R<sub>3</sub> is a polyalkyl group having a weight average molecular weight in the range of about 450 to 5,000; and x is an integer from 0 to 10.

21

22

23

24

2. The compound according to Claim 1, wherein R<sub>1</sub> is hydrogen, hydroxy, or lower alkyl having 1 to 4 carbon atoms; and R<sub>2</sub> is hydrogen.

25

26

27

3. The compound according to Claim 2, wherein R<sub>1</sub> is hydrogen or hydroxy.

28

29

30

4. The compound according to Claim 1, wherein x is 0, 1 or 2.

31

32

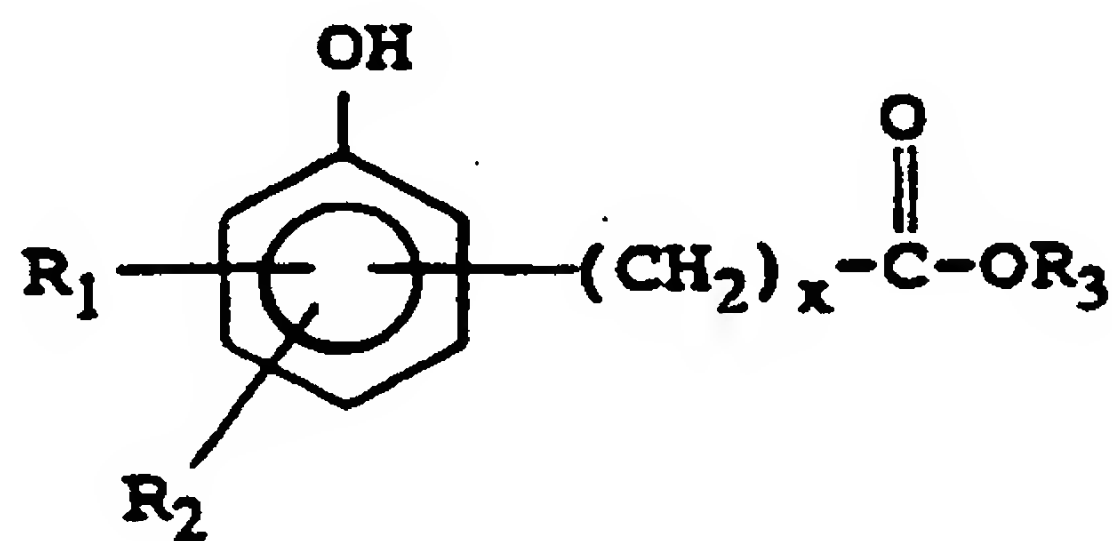
33

5. The compound according to Claim 4, wherein R<sub>1</sub> and R<sub>2</sub> are hydrogen, and x is 0.

34

-31-

- 01 6. The compound according to Claim 1, wherein  $R_3$  is a  
 02 polyalkyl group having a weight average molecular  
 03 weight in the range of about 500 to 5,000.  
 04
- 05 7. The compound according to Claim 6, wherein  $R_3$  has a  
 06 weight average molecular weight in the range of about  
 07 500 to 3,000.  
 08
- 09 8. The compound according to Claim 7, wherein  $R_3$  has a  
 10 weight average molecular weight in the range of about  
 11 600 to 2,000.  
 12
- 13 9. The compound according to Claim 1, wherein  $R_3$  is a  
 14 polyalkyl group derived from polypropylene, polybutene,  
 15 or polyalphaolefin oligomers of 1-octene or 1-decene.  
 16
- 17 10. The compound according to Claim 9, wherein  $R_3$  is  
 18 derived from polyisobutene.  
 19
- 20 11. The compound according to Claim 10, wherein the  
 21 polyisobutene contains at least about 20% of a  
 22 methylvinylidene isomer.  
 23
- 24 12. A fuel composition comprising a major amount of  
 25 hydrocarbons boiling in the gasoline or diesel range  
 26 and an effective detergent amount of a compound of the  
 27 formula:  
 28



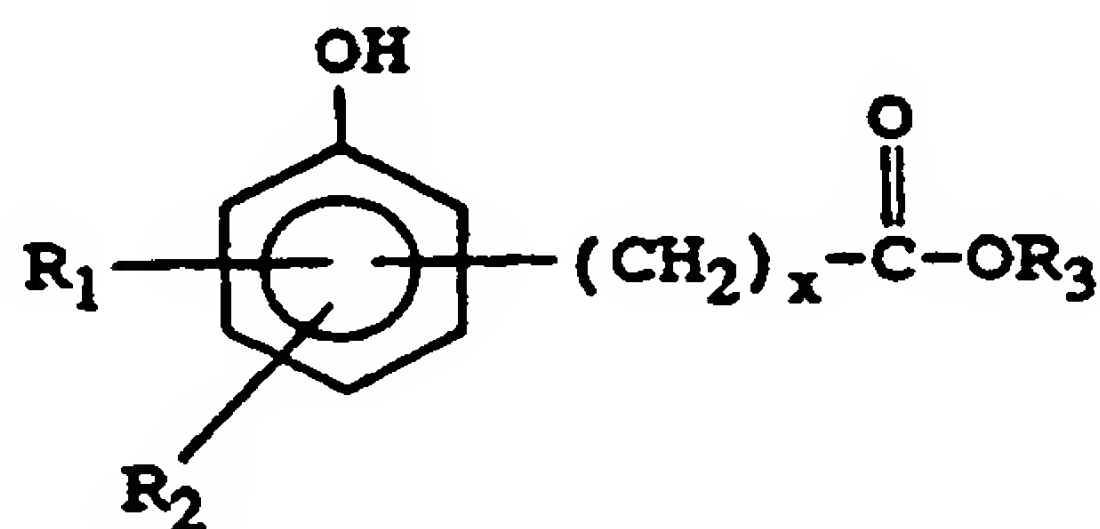


-32-

- 01        or a fuel-soluble salt thereof; wherein  
02  
03         $R_1$  and  $R_2$  are independently hydrogen, hydroxy, lower  
04        alkyl having 1 to 6 carbon atoms, or lower alkoxy  
05        having 1 to 6 carbon atoms;  
06  
07         $R_3$  is a polyalkyl group having a weight average  
08        molecular weight in the range of about 450 to 5,000;  
09        and  $x$  is an integer from 0 to 10.  
10  
11        13. The fuel composition according to Claim 12, wherein  $R_1$   
12        is hydrogen, hydroxy, or lower alkyl having 1 to 4  
13        carbon atoms and  $R_2$  is hydrogen.  
14  
15        14. The fuel composition according to Claim 13, wherein  $R_1$   
16        is hydrogen or hydroxy.  
17  
18        15. The fuel composition according to Claim 12, wherein  $x$   
19        is 0, 1 or 2.  
20  
21        16. The fuel composition according to Claim 15, wherein  $R_1$   
22        and  $R_2$  are hydrogen, and  $x$  is 0.  
23  
24        17. The fuel composition according to Claim 12, wherein  $R_3$   
25        is a polyalkyl group having a weight average molecular  
26        weight in the range of about 500 to 5,000.  
27  
28        18. The fuel composition according to Claim 17, wherein  $R_3$   
29        has a weight average molecular weight in the range of  
30        about 500 to 3,000.  
31  
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-33-

- 01 19. The fuel composition according to Claim 18, wherein  $R_3$   
 02 has a weight average molecular weight in the range of  
 03 about 600 to 2,000.  
 04
- 05 20. The fuel composition according to Claim 12, wherein  $R_3$   
 06 is a polyalkyl group derived from polypropylene,  
 07 polybutene, or polyalphaolefin oligomers of 1-octene or  
 08 1-decene.  
 09
- 10 21. The fuel composition according to Claim 20, wherein  $R_3$   
 11 is derived from polyisobutene.  
 12
- 13 22. The fuel composition according to Claim 21, wherein the  
 14 polyisobutene contains at least about 20% of a  
 15 methylvinylidene isomer.  
 16
- 17 23. The fuel composition according to Claim 12, wherein  
 18 said composition contains about 50 to about 2500 parts  
 19 per million by weight of said compound.  
 20
- 21 24. A fuel concentrate comprising an inert stable  
 22 oleophilic organic solvent boiling in the range of from  
 23 about 150°F to 400°F and from about 10 to about 70  
 24 weight percent of a compound of the formula:  
 25



33 or a fuel-soluble salt thereof; wherein  
 34

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- 01         $R_1$  and  $R_2$  are independently hydrogen, hydroxy, lower  
02        alkyl having 1 to 6 carbon atoms, or lower alkoxy  
03        having 1 to 6 carbon atoms;  
04
- 05         $R_3$  is a polyalkyl group having a weight average  
06        molecular weight in the range of about 450 to 5,000;  
07        and  $x$  is an integer from 0 to 10.  
08
- 09    25.    The fuel concentrate according to Claim 24, wherein  $R_1$   
10        is hydrogen, hydroxy, or lower alkyl having 1 to 4  
11        carbon atoms and  $R_2$  is hydrogen.  
12
- 13    26.    The fuel concentrate according to Claim 25, wherein  $R_1$   
14        is hydrogen or hydroxy.  
15
- 16    27.    The fuel concentrate according to Claim 24, wherein  $x$   
17        is 0, 1 or 2.  
18
- 19    28.    The fuel concentrate according to Claim 27, wherein  $R_1$   
20        and  $R_2$  are hydrogen, and  $x$  is 0.  
21
- 22    29.    The fuel concentrate according to Claim 24, wherein  $R_3$   
23        is a polyalkyl group having a weight average molecular  
24        weight in the range of about 500 to 5,000.  
25
- 26    30.    The fuel concentrate according to Claim 29, wherein  $R_3$   
27        was a weight average molecular weight in the range of  
28        about 500 to 3,000.  
29
- 30    31.    The fuel concentrate according to Claim 30, wherein  $R_3$   
31        has a weight average molecular weight in the range of  
32        about 600 to 2,000.  
33  
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-35-

01 32. The fuel concentrate according to Claim 24, wherein R<sub>3</sub>  
02 is a polyalkyl group derived from polypropylene,  
03 polybutene, or polyalphaolefin oligomers of 1-octene or  
04 1-decene.  
05

06 33. The fuel concentrate according to Claim 32, wherein R<sub>3</sub>  
07 is derived from polyisobutene.  
08

09 34. The fuel concentrate according to Claim 33, wherein the  
10 polyisobutene contains at least about 20% of a  
11 methylvinylidene isomer.  
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## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US94/12363

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C10L 1/18; C07C 69/76, 88

US CL : 44/400; 560/67, 70, 71, 75

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 44/400; 560/67, 70, 71, 75

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US, A, 4,713,475 (SPIVACK ET AL.) 15 DECEMBER 1987, column 1, line 56 to column 2, line 4).	1, 4 and 6-8
Y		9-11
Y	US, A, 3,330,859 (DEXTER ET AL.) 11 JULY 1967, column 1, lines 14-61.	1, 4, 6--24 and 29-34
Y	US, A, 5,206,414 (EVANS ET AL.) 27 APRIL 1993, column 1, lines 43-68; column 16, lines 13-19; column 20, lines 15-24.	1-34

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

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Date of the actual completion of the international search

31 JANUARY 1995

Date of mailing of the international search report

17 FEB 1995

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Commissioner of Patents and Trademarks  
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Washington, D.C. 20431

Facsimile No. (703) 305-3230

Authorized officer

JERRY D. JOHNSON

Telephone No. (703) 308-0661



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